

EUROPEAN PATENT APPLICATION

Application number: 90305114.2

Int. Cl.⁵: G03C 1/08, G03C 1/49,
G03C 5/305

Date of filing: 11.05.90

Priority: 18.05.89 GB 8911453

Date of publication of application:
22.11.90 Bulletin 90/47

Designated Contracting States:
BE DE FR GB IT

Applicant: **MINNESOTA MINING AND
MANUFACTURING COMPANY**
3M Center, P.O. Box 33427
St. Paul Minnesota 55133(US)

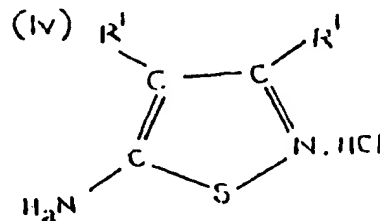
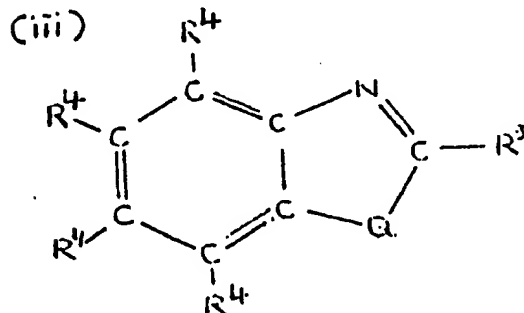
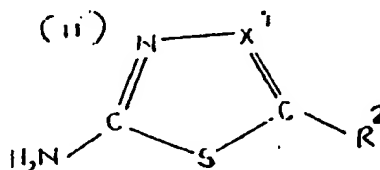
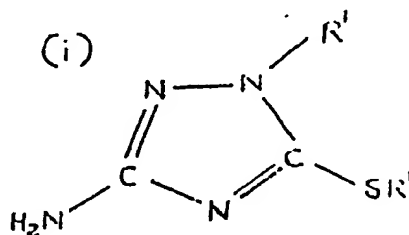
Inventor: **Shor, Steven Michael** c/o Building
209-2C-08

3M Centre, St. Paul
Minnesota 55144(US)
Inventor: **Hall, Kevin Peter** 5 Blacksmiths Way
High Wych, Sawbridgeworth
Hertfordshire(GB)
Inventor: **Slater, Sean Dennis** 16 Old School
Close
Codicote, Hitchin
Hertfordshire(GB)

Representative: **Bowman, Paul Alan** et al
LLOYD WISE, TREGEAR & CO. Norman
House 105-109 Strand
London WC2R OAE(GB)

Speed and contrast promoted silver halide doped emulsions.

Negative-acting silver halide photographic materials comprising Group VIII metal doped silver halide emulsions free from contrast-promoting amounts of hydrazine derivatives containing as speed and contrast promoting agents one or more compounds of the general formula:



EP 0 398 600 A2

The photographic materials are suitable for use in the photolithographic industry and for development of daylight-handleable contact film.

SPEED AND CONTRAST PROMOTED SILVER HALIDE DOPED EMULSIONS

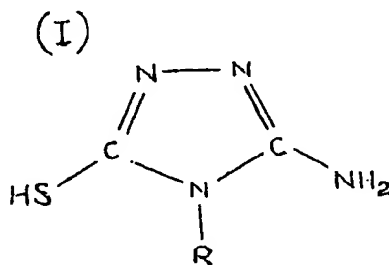
This invention relates to negative-acting silver halide photographic materials and in particular to photographic elements comprising Group VIII metal doped silver halide emulsions associated with a speed and contrast promoting agent which are suitable for use in the photolithographic printing industry and for the development of daylight handleable contact film.

5 Photosensitive silver halide materials are commonly used in the photolithographic industry to obtain half tone, dot or line, high contrast images.

To increase the contrast of lithographic films it is common practice to dope the silver halide emulsions with contrast promoting agents, among which are the water soluble Group VIII metal salts, such as the trivalent salts of rhodium, ruthenium and iridium. It is known that good results as regards high covering
10 power (which is the ratio between the maximum density obtained after development and the silver halide coverage) and rapid developability (for productivity increase) can be obtained by using fine grained (less than 0.15 μm) and high chloride content silver halide emulsions. It is known that such emulsions which contain a Group VIII metal as a contrast promoting agent may still not have the required contrast, and as the dopant desensitises the emulsion, it may not have the required speed.

15 One approach to the development of a daylight handleable contact film has been to modify existing daylight duplicating film. Contact films are negative acting materials which are exposed in contact with an original to record a negative image of the original. Duplicating films are positive acting materials which are exposed in contact with an original to produce an identical copy. To produce a duplicating film, the emulsion is chemically fogged, a metal dopant such as rhodium being required for the reversal process as
20 well as for desensitising purposes. For a contact film, the unfogged duplicating emulsion is far too slow for practical use, primarily due to the level of dopant. As stated previously it is advantageous to have the dopant present for contrast enhancement purposes but to increase the speed and also contrast to usable levels a sensitisation step must be introduced. Conventional gold and sulphur sensitisation does confer some extra speed and contrast but European Patent Applications Nos. 267598 and 138200 and British
25 Patent Applications Nos. 2202341 and 2206700 disclose negative-acting rhodium doped emulsions in which the contrast is enhanced by addition of a hydrazine derivative. Such materials are generally too sensitive to be daylight-handleable, and if this property is required, a desensitiser must be added. Various examples of the latter are disclosed, including 2-mercaptobenzimidazole derivatives.

British Patent No. 741228 discloses the use of 4-substituted 3-amino-5-mercapto-4,1,2-triazoles of
30 general formula (I)



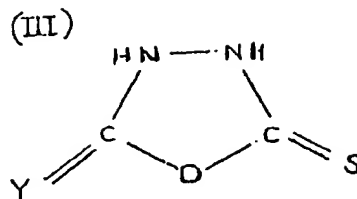
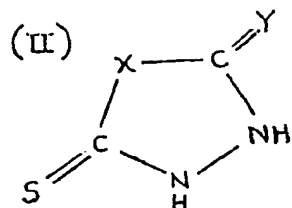
in which:

45 R represents other than H,

in photographic constructions. The compounds of formula (I) are said to restrain the formation of chemical fog without seriously affecting the speed, contrast or other properties of the emulsion.

British Patent No. 2573027 discloses the use of compounds of general formulae (II) and (III)

50



in which:

X represents O or S,

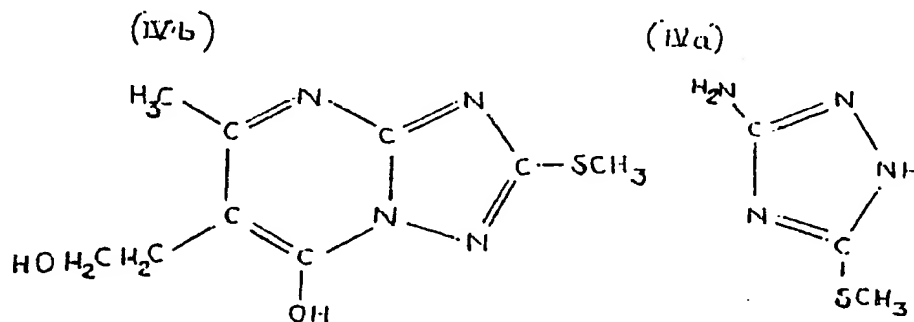
Y represents O, S or NH, and,

D represents substituted or unsubstituted carbon atoms to complete a 6 membered ring,

in a photographic construction as anti-bronzing agents. However, within the patent there is no mention of doping of the emulsions.

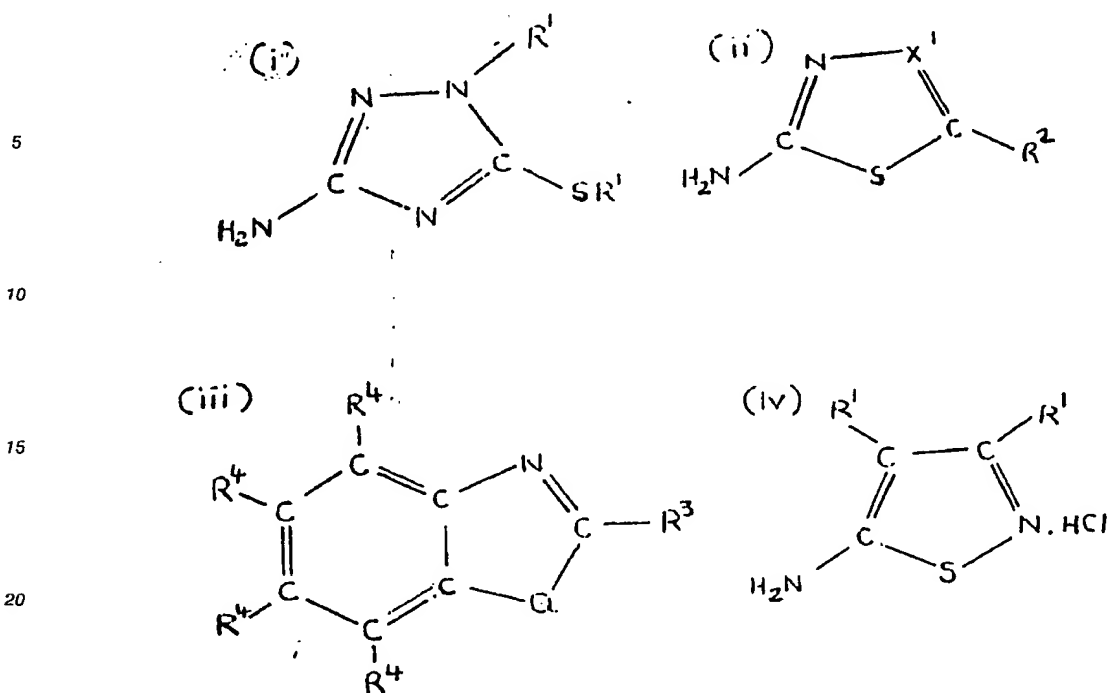
U.S. Patent No. 1,725,934 discloses the use of thiazole derivatives in silver halide constructions, but as an anti-fogging agent.

The combination of a triazole (IVa) and tetrazindene (IVb) is known in the photographic art to act as a stabiliser.



It has now been found that certain groups of compounds, some of which have previously been used as desensitisers, antifoggants, anti-bronzing agents or stabilisers, have a particular utility as speed and contrast promoting agents in Group VIII metal doped, negative-acting silver halide emulsions, the emulsions being chemically-sensitised or otherwise, and being free from contrast-promoting amounts of hydrazine derivatives.

According to one aspect of the present invention there is provided a photographic element comprising a Group VIII metal doped negative-acting silver halide emulsion characterised in that the emulsion is associated with one or more speed and contrast promoting agents comprising a compound having a nucleus of one of the following general formulae (i) to (iv)



in which:

Each R¹ independently represents a hydrogen atom or an alkyl group of 1 to 5 carbon atoms, optionally having one or more substituents selected from hydroxyl moieties, carboxyl moieties, alkoxy carbonyl groups of 1 to 5 carbon atoms, cyano moieties, halogen atoms, nitro moieties, amino moieties and aryl groups of up to 10 carbon atoms, wherein the aryl group may be optionally substituted with one or more substituents selected from alkyl groups of 1 to 5 carbon atoms, hydroxyl moieties, carboxyl moieties, alkoxy carbonyl groups of 1 to 5 carbon atoms, cyano moieties, halogen atoms, nitro moieties and amino moieties,

X¹ represents N or CR⁵, where R⁵ represents R¹ (as defined above) or NO₂,

R² represents a hydrogen atom or SR¹ (R¹ is as defined above) but if X¹ is N then R² is SR¹,

Q represents S or NR¹, in which R¹ is as defined above,

R³ represents an amino group or SR¹ in which R¹ is as defined above, and,

Each R⁴ independently represents R¹ as defined above or a halogen atom, a nitro moiety, a cyano moiety, or an alkoxycarbonyl group of 1 to 5 carbon atoms,

the emulsions being free from contrast-promoting amounts of hydrazine derivatives.

R¹ is preferably a hydrogen atom or a methyl group,

R² is preferably a hydrogen atom or SH,

X¹ is preferably N, -CH, -CCH₃ or -CNO₂,

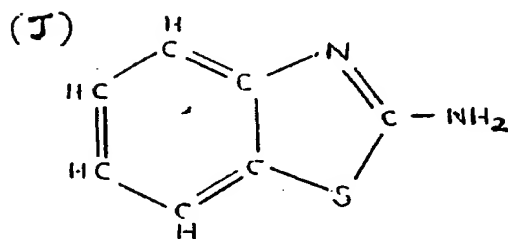
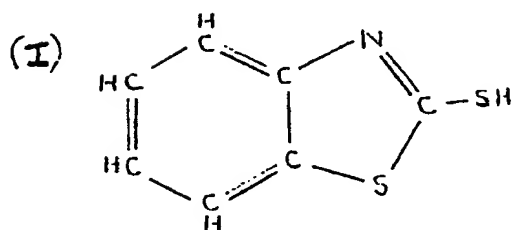
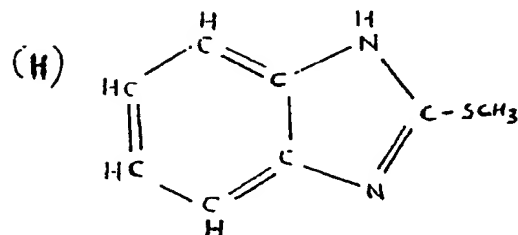
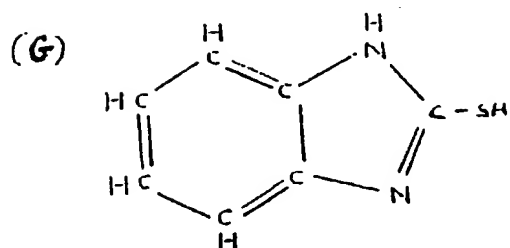
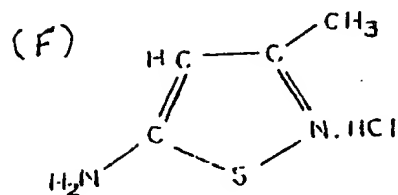
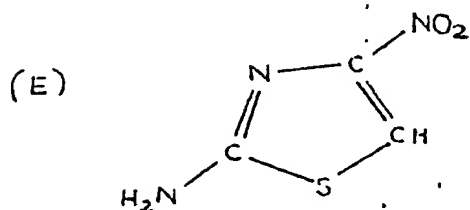
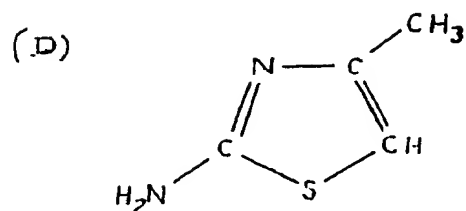
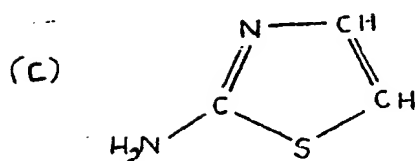
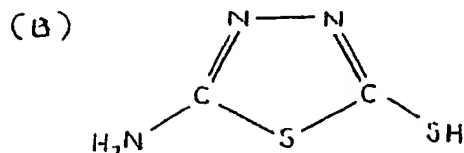
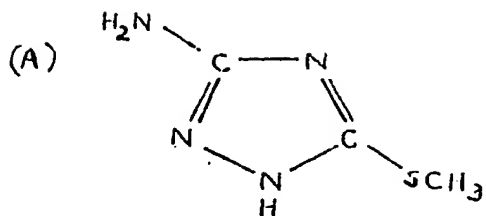
R³ is preferably SH, SCH₃ or NH₂, and,

R⁴ is preferably hydrogen.

The invention provides a negative-acting photosensitive silver halide material which may be used to obtain black and white half tone, line or dot images for photolithographic purposes. The element preferably comprises a support, having one or more hydrophilic colloidal layers located thereon, in which at least one layer comprises a fine grain, high chloride content and Group VIII metal doped photographic emulsion associated with one or more speed and contrast promoting agents selected from compounds of general formulae (i) to (iv).

The speed and contrast promoting agents need not be present in the emulsion during imaging, but must be associated with the emulsion during development. Thus, the compounds of general formulae (i) to (iv) may be introduced in to the emulsion from a treatment bath or the developer solution. The compounds may be present in the photographic element during imaging and optionally additional compounds present in the developer solution.

Examples of compounds suitable for inclusion as speed or contrast promoting agents are:



55 Preferably the fine grain, high chloride content and Group VIII metal doped photographic emulsion is associated with one or more speed and contrast promoting agents selected from compounds A to E.

Conventional sulphur and gold sensitisation is known to confer some extra speed and contrast on these high chloride content rhodium doped photographic emulsions but compounds selected from general

formulae (i) to (iv) yield greater speed and contrast increases than conventional sensitisation methods and can be used in combination with or without a chemical sensitisation step.

After image wise exposure of the fine grain, high chloride content rhodium doped silver halide emulsion, the material undergoes a photographic processing step comprising an alkaline developing solution wherein the speed and contrast promoting agent is reactively associated with the emulsion. In a further embodiment it is also possible to introduce the speed and contrast promoting agent in the developer solution followed by conventional washing or fixing but it is preferred that the agents are introduced as a precoat addition.

The term fine grain is used in the context of the present invention to refer to silver halide grains having an average grain size of not more than $0.2\ \mu\text{m}$. High chloride content refers to the emulsion having at least 60% and preferably at least 80% of its total halide molar content consisting of chloride ions. The emulsion is preferably a chlorobromide emulsion wherein the remainder of the halide content comprises bromide ions and a most preferred emulsion comprises 84% silver chloride : 16% silver bromide having a mean silver halide grain size of $0.09\ \mu\text{m}$.

The term Group VIII metal doped refers to the process whereby during precipitation or physical ripening of the silver halide emulsion, salts of one or more Group VIII metals, e.g., trisodium hexachlororhodate (III), disodium pentachlororuthenate (III) and tripotassium hexachloroiridate (III) are present in the solution. The preferred dopants are water-soluble trivalent salts of rhodium. The speed and contrast increasing effect of the compounds of general formulae (i) to (iv) is directly proportional to the level of dopant. The level of doping may be from 10^{-6} to 10^{-2} moles Group VIII metal salt per mole of silver but preferably is from 10^{-4} to 10^{-2} moles Group VIII metal salt per mole of silver and most preferably from 10^{-3} to 10^{-2} mole Group VIII metal salt per mole of silver.

The amount of the speed and contrast promoting agent added is in the range 10^{-4} to 10^{-1} mole of agent per mole of silver halide but preferably in the range 10^{-2} to 5×10^{-2} mole of agent per mole of silver halide.

The invention will now be described with reference to the following Examples:

EXAMPLE 1

Preparation of a Rhodium Doped Silver Halide Emulsion

A silver halide emulsion of 84 mole % chloride and 16 mole % bromide was prepared by the simultaneous addition under constant agitation of water solution B and water Solution C by the double jet technique over a period of 25 minutes to water gelatin Solution A. The compositions A to C were:

| Solution A | |
|---|---------------------|
| Water | 833.3g |
| Gelatin | 25g |
| Polyvinylpyrrolidone (K-30) | 6.33g |
| KBr | 0.167ml (1N) |
| Solution B | |
| Water | 368g |
| AgNO ₃ | 170g |
| Solution C | |
| Water | 361.3g |
| KCl | 62.65g (0.84 moles) |
| KBr | 19.04g (0.16 moles) |
| Na ₃ RhCl ₆ .12H ₂ O | 0.200g |

The water gelatin Solution A was kept at a constant temperature of 40°C . Solution B was added at a constant addition rate whilst the addition rate of Solution C was varied to maintain the potential of the

emulsion thus formed at a value of $120 \pm 5\text{mV}$ (as measured with a specific electrode for Br ions and a reference electrode of the saturated Ag/AgCl type). The emulsion so prepared, following the removal of soluble salts by the conventional coagulation method, had a mean grain diameter of $0.09\mu\text{m}$. The emulsion was then chemically sensitised with sodium gold chloride and sodium thiosulphate. At the end of the chemical sensitisation a speed and contrast promoting agent selected from compounds A to J in a suitable solvent was added to the emulsion before preparation for coating with the addition of additional gelatin, coating surface active agents and formaldehyde hardener.

The emulsion was coated at a silver coating weight of 2.7g Ag/m^2 onto a polyester support base which was backed with a red antihalation layer.

The resulting films were exposed through a 0-2, 20cm continuous wedge. The exposing lamp was a Violux 1500S UV lamp at a distance of 52 inches from the film plane. The exposed films were developed in 3M RDC™ developer for 20 seconds @ 40°C and fixed in 3M Fix Roll™ Fixer.

The sensitometric data obtained from silver halide coatings made with compounds A to F are illustrated in Table 1 below.

TABLE 1

| Sensitometric Data for Films Containing Representative Examples | | | | | | |
|---|---|------------------------|------------------|-------------------|-----|-----------|
| Compound | Added Amount of Compound (mole/mole AgX) ** | Relative Speed (Log E) | D _{MAX} | Contrast θ | | Exposure* |
| | | | | A | C | |
| None | - | - | 0.11 | - | - | 200 |
| None | - | -4.43 | 1.26 | 0.4 | - | 2000 |
| A | 10^{-2} | -3.46 | 5.1 | 1.5 | 6.0 | 200 |
| B | 2.5×10^{-3} | -3.52 | 5.2 | 1.23 | 6.5 | 200 |
| C | 10^{-2} | -3.53 | 3.6 | 1.27 | 5.4 | 200 |
| D | 10^{-2} | -3.50 | 4.2 | 1.35 | 5.4 | 200 |
| E | 10^{-2} | -3.60 | 5.3 | 1.44 | 6.5 | 200 |
| F | 10^{-2} | -3.78 | 2.8 | 0.95 | 2.8 | 200 |

* Exposure on a Violux UV lamp (as described previously)

** Generally the amount added to give maximum effect is listed.

Contrast A is measured between densities 0.07 and 0.17 above D_{min}.

Contrast C is measured between densities 0.5 and 2.5 above D_{min}.

Each of compounds A to F were dissolved in an appropriate solvent and added at varying levels as a precoat addition to the emulsion. The emulsion used had the composition described previously and had been chemically sensitised with conventional sulphur and gold compounds. When no speed and contrast enhancing compound is added and with conventional exposure and processing the film shows little development, only on extremely long exposures to UV light does any density build up. However, when the compounds of the invention are added, then a dramatic speed and contrast increase is seen.

EXAMPLE 2

Effect of Varying the Halide Ratio of the Emulsion

An alternative to the emulsion composition described in Example 1 was tested with Compound A. The emulsion was made following the protocol described previously except the halide ratio was altered from 84 : 16 chloride to bromide to 96 : 4. Very similar results were observed with increases in both speed and contrast.

EXAMPLE 3

5

Effect of Compound A as a Developer Addition

Some digested emulsion (composition as per Example 1) was coated in the standard fashion with no addition of any of the speed or contrast promoting agents. The film was given the standard exposure and
 10 processed in RDC developer having some of compound A added. Washing and fixing were carried out in a conventional fashion.

At high levels of A, boosts in speed and contrast were observed but greater effects were noticed when A was added as a precoating addition.

15

EXAMPLE 4

20

Effect of Varying the Rhodium Dopant

25

Level in the Emulsion

To investigate whether the effect of the compounds of the present invention was also a function of the rhodium dopant level in the emulsion the following emulsions were made and coated as described below:

Emulsion 1 as detailed previously for Example 1.

30 Emulsion 2 exactly the same as Emulsion 1 except 0.0421g of $\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$ was used. Emulsion 3 exactly the same as Emulsion 1 except $4.21 \times 10^{-3}\text{g}$ of $\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$ was used.

Emulsion 4 exactly the same as Emulsion 1 except that no rhodium was used.

The exposure was varied depending on the speed of the coated emulsions. The greater the level of rhodium, the slower the film is and hence, a greater exposure period is required. Emulsion 4 was found to
 35 be too fast to be exposed by the Violux UV lamp so exposure was conducted with a quartz lamp.

For each emulsion, four coatings were made as described in Table 2.

TABLE 2

40

| Coating Design. | Chemically Digested | Compound A* |
|-----------------|---------------------|-------------|
| I | No | No |
| II | Yes | No |
| 45 III | No | Yes |
| IV | Yes | Yes |

*400ml per mole of a 0.325% solution of Compound A.

50

The following Tables show the increase in speed (measured at a density of 1), toe and shoulder contrast (measured between 0.07 and 0.17 and 0.5 and 2.5 above D_{min} respectively) that occurred on addition of Compound A for undigested and chemically sensitised emulsions (i.e. sulphur and gold sensitised).

55

TABLE 3

| Increase in speed (logE) on addition of Compound A | | |
|--|------------------------|---------------------------------|
| Emulsion | Chemical Sensitisation | |
| | No | Yes |
| 1 | * | + 0.78 highest level of rhodium |
| 2 | * | + 0.55 |
| 3 | +0.8 | + 0.5 |
| 4 | +0.07 | + 0.4 no rhodium |

*In these cases the coatings of the undigested emulsion with no Compound A were too slow to be measured using the same exposure level. For emulsion 1 the speed increase is estimated to be $> 2\log E$ for the undigested emulsion.

TABLE 4

| Increase in toe contrast (O_A) on addition of Compound A | | |
|--|------------------------|-------|
| Emulsion | Chemical Sensitisation | |
| | No | Yes |
| 1 | * | +2.0 |
| 2 | * | +1.1 |
| 3 | +0.7 | +0.5 |
| 4 | +0.15 | +0.14 |

TABLE 5

| Increase in shoulder contrast (O_C) on addition of Compound A | | |
|---|------------------------|------|
| Emulsion | Chemical Sensitisation | |
| | No | Yes |
| 1 | * | +9.8 |
| 2 | * | +6.0 |
| 3 | +2.9 | +3.2 |
| 4 | +0.6 | +0.6 |

TABLE 6

| Increase in speed (logE) on Chemical Sensitisation | | |
|---|------------|--------------------------------|
| Emulsion | Compound A | |
| | None | Added as a precoating final |
| 1 | - | +0.2 |
| 2 | - | +0.2 |
| 3 | +0.6 | +0.3 |
| 4 | +0.4 | +0.72 |

From Tables 3 - 6 it can be seen that the addition of Compound A causes a large increase in speed to both undigested and chemically sensitised emulsions. The effect is greater for the undigested emulsion and for emulsions containing the higher levels of rhodium dopant.

The same observations hold for the toe and shoulder contrasts (Table 4 and Table 5 respectively).

Table 6 shows the increase in speed (logE) observed on chemical sensitisation when Compound A is added as a precoating addition or not added at all. It can be seen that with no Compound A present, digestion gives a greater increase in speed with increasing levels of rhodium dopant, when Compound A is added as a final the effect of chemical sensitisation decreases with increasing rhodium dopant level i.e. at higher rhodium levels most of the speed increase comes from the addition of Compound A, the digestion step only gives a small further speed increase.

EXAMPLE 5

Effect of various Group VIII dopants

An emulsion similar to that in Example 1 was prepared except that the halide ratio was adjusted so that it was 96 mole % chloride 4% bromide emulsion. Seven emulsions were prepared with the following levels of Group VIII transition metal dopants.

Emulsion 1 no dopant.

Emulsion 2 $\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$ 0.014g per mole of silver.

Emulsion 3 $\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$ 0.14g per mole of silver.

Emulsion 4 $\text{Na}_2[\text{RuCl}_5(\text{H}_2\text{O})]$ 0.0093g per mole of silver.

Emulsion 5 $\text{Na}_2[\text{RuCl}_5(\text{H}_2\text{O})]$ 0.093g per mole of silver.

Emulsion 6 K_3IrCl_6 0.013g per mole of silver.

Emulsion 7 K_3IrCl_6 0.13g per mole of silver.

Once prepared the emulsion was washed and chemically sensitised in the same way as in Example 1. Compound A was then added at a level of 1.95g per mole of silver. The emulsion was then coated onto clear subbed polyester with the conventional coating aids and hardeners at a coating weight of 2.5g Ag/m^2 .

The resulting films were exposed through a 0-4 10cm continuous wedge. The exposing source was a Thieme Spektra Proof Daylight containing a 1KW Th1007 polymer bulb. The exposed films were developed in 3M RDC developer for 30 seconds at 35°C and fixed in 3M Fix Roll fixer.

The sensitometric data obtained are given in Table 7. Two different coatings of each emulsion were made using the following design:

| Type | Chemical Sensitisation | Compound A |
|------|------------------------|------------|
| i) | yes | absent |
| ii) | yes | present |

TABLE 7

| Emulsion | Type | Rel. speed/log E | Maximum Density | Contrast | Exposure/Units |
|----------|------|------------------|-----------------|----------|----------------|
| 1 | i) | 3.1 | 4.2 | 4.5 | 1 |
| | ii) | 3.2 | 4.2 | 5.3 | 1 |
| 2 | i) | 1.9 | 4.4 | 4.6 | 4 |
| | ii) | 2.2 | 4.4 | 12.2 | 4 |
| 3 | i) | .3 | 1.3 | - | 4 |
| | ii) | .9 | 4.2 | 9.3 | 4 |
| 4 | i) | 2.6 | 2.7 | 0.7 | 4 |
| | ii) | 2.9 | 4.2 | 5.6 | 4 |
| 5 | i) | 1.2 | 1.3 | - | 4 |
| | ii) | 1.4 | 4.2 | 2.4 | 4 |
| 6 | i) | 2.6 | 4.4 | 4.8 | 4 |
| | ii) | 2.7 | 4.4 | 6.7 | 4 |
| 7 | i) | 1.8 | 3.4* | 4.8 | 4 |
| | ii) | 2.1 | 4.3 | 6.7 | 4 |

* Strong solarisation noticed. Speed measured at 1.00 above fog. Contrast measured between 0.5 and 2.5 above fog.

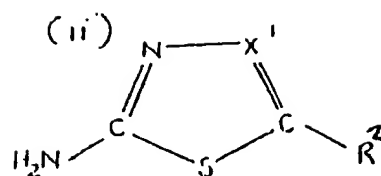
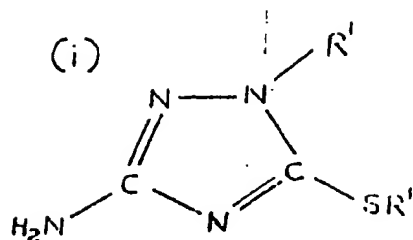
Comparison of the results for the rhodium doped Emulsions 2 and 3 with the undoped Emulsion 1 show the significant effect of Compound A. Improvements in speed and contrast are obtained, the magnitude of the improvement related directly to the level of rhodium dopant. A large increase in maximum density is also observed for Emulsion 3. They also show the overall desensitisation effect of rhodium.

For the ruthenium doped Emulsions 4 and 5 improvements in speed and, especially, contrast and maximum density are again obtained on addition of Compound A. Emulsions 6 and 7 show the effect of iridium doping. There is an overall desensitisation related to the level of dopant (see li) 6i) and 7i). On addition of Compound A speed, contrast and for the heavily doped emulsion maximum density are increased. For Emulsion 7 solarisation is also observed which is eliminated on addition of Compound A.

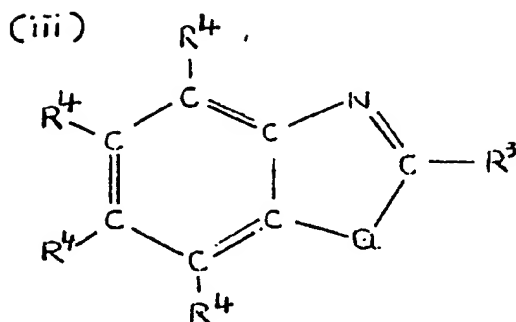
Claims

1. A photographic element comprising a Group VIII metal doped negative-acting silver halide emulsion characterised in that the emulsion is associated with one or more speed and contrast promoting agents comprising a compound having a nucleus of one of the following general formulae: (i) to (iv)

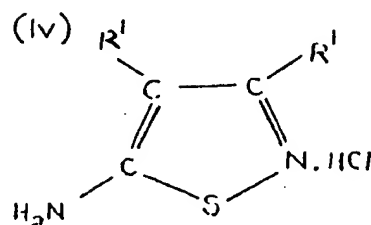
5



10



15



20

in which:

Each R¹ independently represents a hydrogen atom or an alkyl group of 1 to 5 carbon atoms, optionally having one or more substituents selected from hydroxyl moieties, carboxyl moieties, alkoxy carbonyl groups of 1 to 5 carbon atoms, cyano moieties, halogen atoms, nitro moieties, amino moieties and aryl groups of up to 10 carbon atoms, wherein the aryl group may be optionally substituted with one or more substituents selected from alkyl groups of 1 to 5 carbon atoms, hydroxyl moieties, carboxyl moieties, alkoxy carbonyl groups of 1 to 5 carbon atoms, cyano moieties, halogen atoms, nitro moieties and amino moieties,

X¹ represents N or CR⁴, where R⁴ represents R¹ (as defined above) or NO₂,

R² represents a hydrogen atom or SR¹ (R¹ is as defined above) but if X¹ is N then R² is SR¹,

Q represents S or NR¹ in which R¹ is as defined above,

R³ represents an amino group or SR¹ in which R¹ is as defined above, and,

Each R⁴ independently represents R¹ as defined above or a halogen atom, a nitro moiety, a cyano moiety, or an alkoxy carbonyl group of 1 to 5 carbon atoms, the emulsion being free from contrast-promoting amounts of hydrazine derivatives.

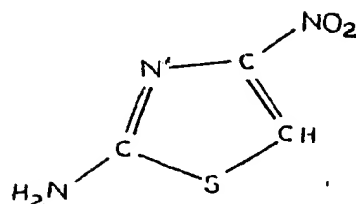
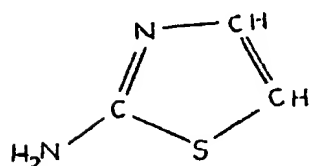
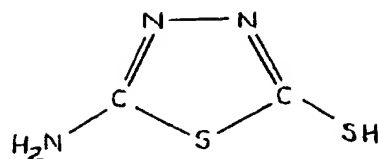
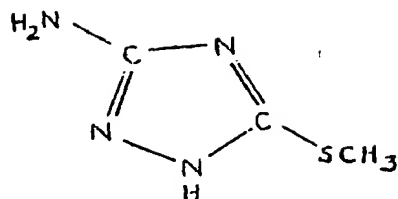
2. A photographic element as claimed in Claim 1 characterised in that the Group VIII metal dopant is rhodium.

3. A photographic element as claimed in Claim 1 or Claim 2 characterised in that the speed and contrast promoting agent is a compound selected from:

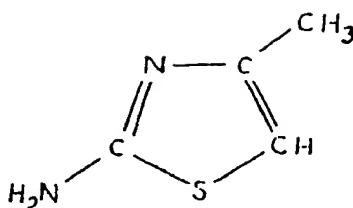
45

50

55



and,



4. A photographic element as claimed in any preceding claim characterised in that the silver halide emulsion comprises a support upon which is coated one or more hydrophilic colloidal layers in which at least one layer comprises a fine grain silver halide emulsion having an average grain size of not more than 0.2 μm .

5. A photographic element as claimed in Claim 4 characterised in that the silver halide emulsion comprises a chlorobromide emulsion in which silver chloride comprises at least 60% of the total silver halide content.

6. A photographic element as claimed in any preceding claim characterised in that the speed and contrast promoting agent has a concentration of 10^{-4} to 10^{-1} moles per mole of silver halide.

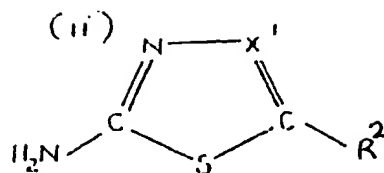
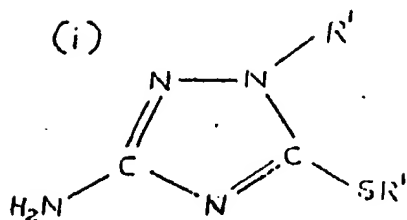
7. A photographic element as claimed in any preceding Claim characterised in that the concentration of Group VIII metal dopant is from 10^{-5} to 10^{-2} moles dopant per mole of silver halide.

8. A photographic element as claimed in any preceding claim characterised in that the dopant comprises a water soluble trivalent rhodium salt.

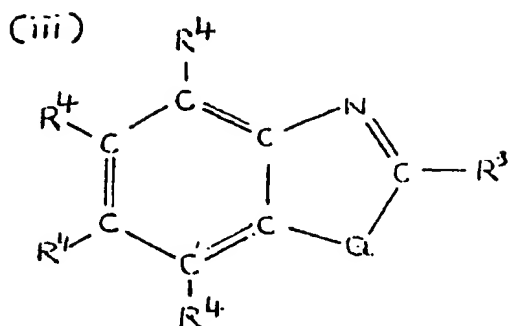
9. A photographic element as claimed in any preceding Claim characterised in that the silver halide emulsion is sulphur and gold sensitised.

10. A photographic process which comprises image wise exposing a photographic element comprising a Group VIII metal doped negative acting silver halide emulsion free from contrast-promoting amounts of hydrazine, developing and fixing said exposed element characterised in that one or more speed and contrast promoting agents is associated with the emulsion during development, said agent being selected from compounds having a nucleus of one of the general formulae:

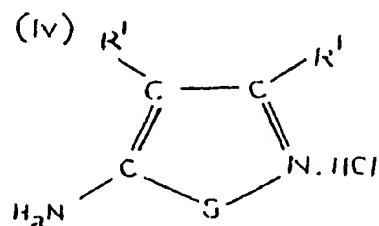
5



10



15



20

in which:

R¹ to R⁴, X¹ and Q are as defined in Claim 1.

25

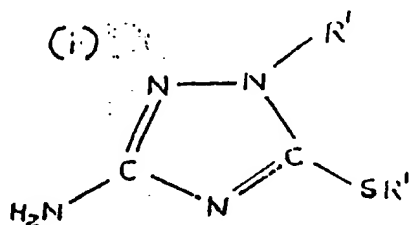
11. A photographic process as claimed in Claim 10 characterised in that the speed and contrast promoting agent:

- (i) is present in the emulsion prior to exposure, and/or,
- (ii) is introduced into the emulsion after exposure, and/or,
- (iii) is present in the developer solution.

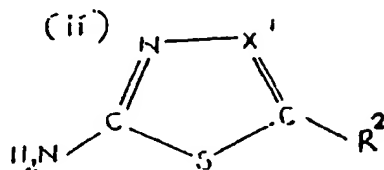
30

12. A developing solution for a photographic element characterised in that the developing solution comprises one or more speed and contrast promoting agents of formula:

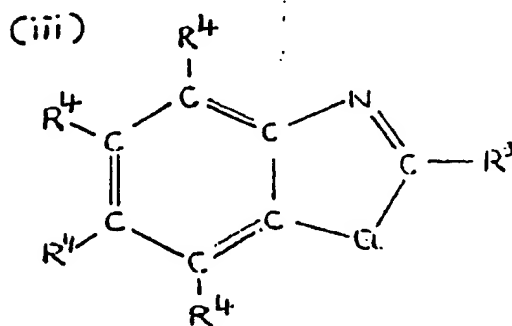
35



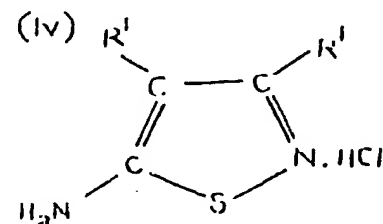
40



45



50



55

in which:

R¹ to R⁴, X¹ and Q are as defined in Claim 1.